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AMBIENT AIR ANALYSIS WITH A
THERMAL DESORPTION / GAS CHROMATOGRAPH / MATRIX ISOLATION /
INFRARED SPECTROMETER SYSTEM

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INTRODUCTION

The detection and measurement of organic compounds in the ambient air by the staff at the Air Resources Branch of the Ontario Ministry of the Environment is presently accomplished by a gas chromatograph / mass selective detector system (GC/MSD). Organic airborne contaminants are collected on and thermally desorbed from a glass cartridge containing three layers of adsorbent materials, and then injected into the GC. The sample is split into three streams: two streams pass through capillary columns (of different polarity) to flame ionization detectors (FID); the other stream passes through a capillary column to the mass selective detector for generation of the mass spectra of the individual compounds. Compound identification is made by comparing the mass spectra to a library of known mass spectra, and by comparing the retention indices for the compounds (on the two columns connected to FIDs) to a user-generated library of known retention indices. Concentrations are determined by calibrating the GC system with standard injections and comparing the peak areas.

In some cases GC/MSD is not sufficient for complete characterization of the GC eluate due to the inability of the MSD to distinguish between certain isomers. Comparison of infrared spectra (IR) is a complementary technique to the MSD usage that can significantly improve the confidence and number of compound identifications in a sample. Until the last few years the IR method was relatively insensitive compared to mass spectrometry (MS); however the recent commercial introduction of a matrix isolation (MI) interface between a GC and a Fourier transform infrared (FT-IR) spectrometer has changed that relationship. The GC/MI/FT-IR system captures the compounds eluting from the GC column in an IR transparent matrix of solid argon at a temperature of 12K. The separated compounds can then be scanned with the FT-IR spectrometer for indefinite periods. Good quality MI/FT-IR spectra can be obtained for most organic compounds with less than 10 nanograms (10^{-9} gm), while the more polar molecules may be seen at levels of only 50 to 100 picograms (10^{-12} gm).

In addition to the equivalent sensitivity to MS, the MI/FT-IR spectra have very sharp features due to the extremely low temperature of the argon cage, the limited rotational motion of the trapped molecules, and the lack of intermolecular effects (argon:analyte ratio is approximately 1000:1). The simplified spectra with sharp features will usually ensure that different isomers can be easily distinguished.

The objective of this study was to evaluate thermal desorption of cartridges as an effective means of introducing air samples to the GC/MI/FT-IR system.

GENERAL DESCRIPTION OF THE METHOD

Ambient air samples were collected on three-layer adsorbent cartridges connected to Gilian samplers operating usually at a sample flow of 100 mL/min for 60 minutes, thereby giving a six litre sample. The adsorbents used were Carbotrap B, Carbotrap C and Spherocharb - each layer was about 2 cm long in the 7 mm id glass cartridge, separated and held in place by plugs of quartz wool. The loaded cartridge was loaded into a thermal desorption system (CRYOTHERM 8901) built by an instrument specialist at the Air Resources Branch. The cartridge was heated to 300 C for 7 minutes under a helium flow of 10 mL/min, thereby driving all contaminants through a Nafion dryer onto a short length (7 cm) of nickel capillary tubing (the "loop"), being cooled to a temperature of -180 C at one end and about -50 C at the other. The cold loop served to focus the contaminants into a small plug, which was then ballistically heated for 12 seconds under GC carrier gas purge (helium) and driven onto the head of the GC column for the start of the GC analysis. Figure 1 outlines the method.

The sample components passed through the GC column to a splitter which sent about 20 % to the FID and 80 % to an open-split interface, where the argon matrix gas was added to the eluate and then sent down the transfer line (240 C) to the slowly rotating cold disk (12 K, 10^{-5} torr). A solid argon track was formed on the disk surface with the eluted compounds embedded sequentially along its length according to their retention time on the GC column. The disk was then rotated 180 degrees to position the track in the optical path of the FT-IR spectrometer. The track was slowly stepped through the optical path, with the total IR absorbance measured at each step, to produce an IR chromatogram of the GC analysis. This IR chromatogram (PSIR) was used together with the FID chromatogram to decide where to collect IR spectra along the track. An example of both chromatograms is shown in Figure 2.

RESULTS AND DISCUSSION

The first test of the new desorption unit was to see how effective it was in desorbing cartridges spiked with a standard mixture of organic compounds. In comparison with standard injections at port #2 of aromatic and chlorinated organics, the peak areas and GC chromatograms were essentially identical. Redesorption of the same cartridge showed no residual peaks.

What else was trapped on the cartridge during sampling and then desorbed? Carbon dioxide and water were also seen in all samples in relatively large amounts. Fortunately they are both small molecules with fairly simple MI/IR spectra at 12K, so their characteristic absorption bands could often be subtracted from the sample spectra without problems.

Dryer

Several procedures were tried in order to minimize the water (important) and carbon dioxide effects on the system. The trapping of large amounts of water was expected, so the desorber was designed to include a Nafion dryer in-line between the cartridge and the cold "loop". Published results on Nafion dryer investigations also suggested that conditioning the dryer between samples by heating it up to 100 C, with purging gas, and cooling it down to ambient temperature, would improve the water removal effectiveness by a factor of 20.

RESULT: Based on visual comparison of the water droplets formed on the cartridge walls during the desorption step to the ice crystals formed on the cold disk during the GC analysis, the Nafion dryer is very effective in removing more than 90 % of the water.

GC oven temperature program

The standard procedure at the ARB lab was to start the GC analysis at an oven temperature of -60 C and ramp it up to 200 C at 10 /min. That temperature program in the present study led to a broad water peak covering the 3-10 minute period in the eluate, although only noticeable in the IR chromatogram and not in the FID response. A procedure that has met with some success was to start the GC analysis at oven temperature of +20 C, hold for 3.0 minutes, and then ramp at whatever rate desired.

RESULT: Holding the GC oven temperature at +20 C for the first 3.0 minutes focused both the carbon dioxide and the water into relatively narrow plugs that were mostly eluted by that time, allowing fairly clean spectra for compounds eluting after pentane (retention index = 500). Different conditions may be necessary to get clear results for the compounds eluting earlier.

Tenax GC

Another possibility that was investigated was to make a cartridge with Tenax GC as the adsorbent, and test the claim that it is hydrophobic, i.e. does not trap water.

RESULT: More than twice the usual amount of water was desorbed from the Tenax GC cartridge - visual observation only. The conclusion was that the present cartridge was satisfactory for now.

Quartz Wool

Ambient air samples spiked with standard injections were collected on cartridges packed only with quartz wool to determine if the water, carbon dioxide or the organics were being trapped on it to any extent, instead of completely on the three layers of adsorbents.

RESULT: The desorbed cartridges showed that nothing had been trapped on the quartz wool, making it entirely neutral in the adsorption/desorption process.

Ambient Samples

Ambient air samples were collected in the downtown Toronto area during July and August, in duplicate, by adjacent Gilian samplers operating at 100 mL/min for 60 minutes in most cases. One set of the cartridges was analyzed on the existing GC/MSD system at ARB. The other set was analyzed on the GC/MI/FT-IR system.

Attention was focused on 11 compounds (Table 1) from the target list of 22 compounds currently used at the ARB mobile support laboratory. MI/FT-IR spectra were obtained for each compound, baseline-corrected, then computer searched with a squared difference algorithm against a user-generated library of about 180 MI/FT-IR spectra and a commercial library of 5000 MI/FT-IR spectra (if necessary). Each spectral search with the small library took about 1.5 seconds, the large library about 1.5 minutes.

Identification

Identification by IR was considered accurate if a clear #1 choice was listed in the hit list or if all of the major spectral features were superimposable between the sample spectrum and the library spectrum. In all cases, if a sufficient amount of the compound was present, the #1 choice was clear or a quick visual comparison of the spectral features for the top 10 choices would determine the identity.

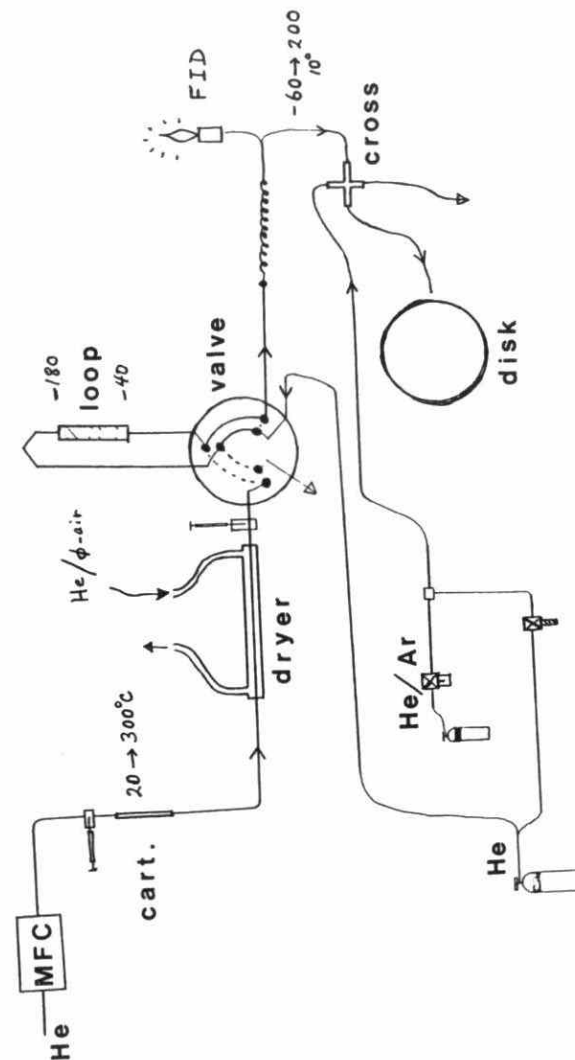
The operator of the GC/MSD system found a similar situation for the other sample set. A sufficient amount of material usually produced a #1 hit or it could be determined by quickly scanning visually through the top 10 choices. One of the uncertain areas, as expected, was distinguishing the xylene isomers.

Concentration

Although the primary strength of the GC/MI/FT-IR technique is unambiguous identification of the compounds, an initial attempt was made in this study to determine some concentrations based on the IR absorbance of one of the main spectral features for each compound - usually the largest one. Based on four replicate injections of a low concentration standard mixture, and assuming the Beer-Lambert to be true, the concentrations of the 11 target compounds were calculated for some of the ambient samples and compared with results from the GC/MSD system. In general the results were in quite good agreement and will be presented.

Other Results

There were a few samples taken in support of the mobile air monitoring units (MAMU) during their ambient air surveys in Ontario. Some of those findings will also be presented.



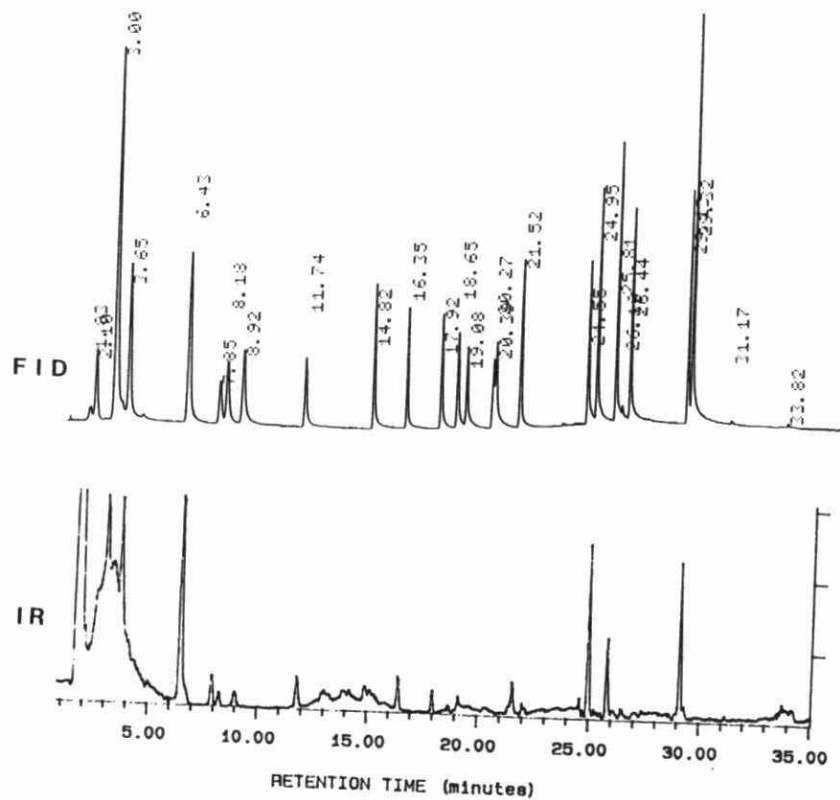


Figure 2 Chromatograms



TABLE 1

Target Compounds	Retention Time (min.)
1,1,1-trichloroethane	7.84
benzene	8.91
trichloroethene	11.74
toluene	14.82
tetrachloroethene	16.35
ethylbenzene	18.66
m,p-xylene	19.06
o-xylene	20.38
1,2,4-trimethylbenzene	24.55
1,2,4-trichlorobenzene	29.13
naphthalene	29.34

Note 1. Retention times based on a GC oven temperature program of: hold at +20C for 10 min., 10 deg/min up to 73C, hold for 5 min, and 10 deg/min up to 200C



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